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The Effect of Chrome Adhesion Layer on Quartz Resonator Aging

Kurt O. Wessendorf and James A. Ohlhausen

Prepared by
Sandia National Laboratories
Albuquerque, New Mexico 87185 and Livermore, California 94550

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Kurt O. Wessendorf, Org. 01732
P.O. Box 5800, MS0525
Sandia National Laboratories
Albuquerque, NM 87185-0525

James A. Ohlhausen, Org. 01822
P.O. Box 5800, MS0886
Sandia National Laboratories
Albuquerque, NM 87185-0886

ABSTRACT

This SAND report documents a late start LDRD designed to determine the possible aging effects of a quartz resonator gold adhesion layer. Sandia uses quartz resonators for applications. These applications require a very stable frequency source with excellent aging (low drift) characteristics. These parts are manufactured by one of our qualified vendors outside Sandia Laboratories, Statek Corp. Over the years we, Sandia and the vendor, have seen aging variations that have not been completely explained by the typical mechanisms known in the industry. One theory was that the resonator metallization may be contributing to the resonator aging. This LDRD would allow us to test and analyze a group of resonators with known differentiating metallization and via accelerated aging determine if a chrome adhesion layer used to accept the final gold plating may contribute to poor aging. We worked with our main vendor to design and manufacture a set of quartz resonators with a wide range of metallization thickness ratios between the chrome and gold that will allow us determine the cause of this aging and which plating thickness ratios provide the best aging performance while not degrading other key characteristics.

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INTRODUCTION

Sandia uses quartz resonators for many applications that require high precision frequency references our weapon applications. These applications require a very stable frequency source with excellent aging (low drift) characteristics. State-of-the-art, low aging quartz resonator designs use cold-weld metal can packages to achieve the lowest possible aging characteristics. Most of the applications that Sandia is designing are for advanced weapon applications which require surface mount packages that have historically been difficult to manufacture and obtain the lowest aging performance. In particular we use a miniature, ceramic surface-mount resonator manufactured by Statek Corp. The low-profile ceramic package lidding process uses a high-temperature solder-seal between the metalized package and lid. Some of this aging is most likely due to low level contamination occurring in the sealing process. Contamination and or a leak in the package causes mass accumulation on the resonator surface resulting in negative frequency change over time. To obtain the best possible aging characteristics for our requirements we pre-age the resonators over time at high- temperature (approx 100 C) to force the resonator/package to stabilize. This aging both stabilizes the parts and provides data with which one can select the most desirable aging rates for the deliverables. Over the years we have used this component Sandia and the vendor have observed aging variations that have not been explained by the typical mechanisms known in the industry. A life extension project on this component has led us to believe that maybe the thickness and interaction of the plated metals on the quartz surface could contribute to the resonator aging characteristics. It was previously thought that the chrome (Cr) adhesion layer migration through the gold (Au) and subsequent oxidation may explain the variability we see. This LDRD was designed to allow us to test and analyze a group of resonators with known differentiating metallization and via accelerated aging determine the true cause of this variability. We work with Statek Corp. to design and manufacture a set of quartz resonators with a wide range of metallization thickness ratios between the Cr and Au that will allow us to determine if the cause of this aging and which plating thickness ratios provide the best aging performance while not degrading other key characteristics. Figure 1 shows typical aging characteristics of quartz resonators. Curve A (t) shows a positive frequency shift with time. This response is attributed to resonator stress relief. Curve B (t) is a negative frequency characteristic that is attributed to mass increase on the resonator surface. This is typically caused by contamination and or adhesives out-gassing from inside the package onto the resonator surface. The third curve is simply a combination of the two responses. The Statek surface mount resonators typically behave like curve B (t) and can vary relatively wide in aging rate. To use these resonators the resonators are aged over many weeks at elevated temperature (approx. 100 C) forcing the resonator to become more stable over time due to a decreasing aging rate over time.

Figure 1: Typical quartz-resonator aging characteristics.

BACKGROUND

AT cut crystal resonators consist of a plate of quartz (usually rectangular or disc-shaped) with an electrode region on each side (again, usually rectangular or disc-shaped). Ideally these electrodes would present no stress or other effects that could cause the resonator's frequency to change over time. Historically, gold has become the electrode material of choice. Gold is highly conductive, presents minimal stress on the resonator, and stable in that it does not oxidize (unlike most metals). Unfortunately, gold by itself does not firmly adhere to quartz. A weakly bonded film of gold would easily pull away from the quartz wafer surface, thereby, exposing bare quartz that would be etched away during the resonator quartz milling process used in this design. Also, a gold only electrode would be so weakly attached that the gold would actually come loose from the resonator under high drive level operation dramatically changing the resonant frequency.

To avoid this problem, a thin layer of chrome is first deposited on the quartz wafer and then the gold is deposited on the chrome layer. In this way, the chrome is used as a "glue" to adhere the gold the quartz wafer. This works very well, but there are a few drawbacks to the use of chrome. Firstly, chrome has a much lower conductivity than gold. By itself this wouldn't be a problem, but it turns out that through exposure to high temperatures some of the chrome can diffuse into the gold thereby increasing the resistance of the electrode and so increasing the resistance of the resonator. Secondly, chrome oxidizes easily. Were the chrome contained between the quartz wafer and the gold film, this wouldn't be an issue, but again the chrome can diffuse into the gold. And if it reaches the surface of the gold film, there is the potential that it could oxidize (if oxygen is present). For these reasons, it is generally thought that the less

chrome used the better. Use enough so that the gold film adheres sufficiently well to the quartz wafer, but no more.

Statek Corporation's standard A (t) resonator processing uses a chrome thickness of 250 Å (25 nm). Here we've looked at the effect of this chrome thickness on the frequency aging of some Statek CX1 20.0 MHz crystals. For these we had three groups of crystals manufactured: one group with 100Å chrome layer; one group with a 250Å chrome layer (Statek's standard); and another group with a 450Å nm chrome layer. Figure 2 shows examples of the Statek resonator.

Figure 2. Statek Corporation surface mount resonators.

EXPERIMENT METHODOLOGY

The Sandia vendor manufactured and delivered three groups of resonators that were made with three different Cr adhesion layer thicknesses and tuned all the resonators to the specification with the top final Au layer. The Cr adhesion layers were selected to be 100, 250 and 450 angstroms. Each group was made with the same processes and thirty of each group was aged in a standard resonator tester manufactured by Sauders Corp. The frequency reference was maintained by an atomic clock standard to assure measurement precision. Measurements for aging characteristics require sub-ppm (parts per million) frequency measurements because over this test one could be trying to measure < 1 ppm over the whole experiment. The resonators were aged for approximately two weeks at 105 degrees C for 20 hours a day. The resonators were measured daily after a four hour soak at 70 degrees C which is the turn-over temperature for these devices. The turn-over temperature is where the resonator derivative of frequency to temperature is approximately zero. The resonator frequency to temperature slope at 105 C is very high and small errors in temperature control will result in large frequency deviations. Measuring the resonator at turn-over temperature minimizes the effect of small temperature deviations from impacting the frequency measurement. Figure 3 shows typical frequency vs. temperature curves for AT-cut resonators.

The resonators used in this test were similar to the 35 degrees and 18 minute curve shown here, note the relatively flat slope at 70 C.

Figure 3: AT- Cut resonator, frequency vs. temperature.

After the measurement cycles were complete the resonator frequency change versus time was graphed to determine if there were differences in the groups and how large these differences were. Figure 4 shows the data collected on the aged units over the fifteen day test. Also a surface analysis was done on the best, nominal and worst performance examples of each group to determine if there were any significant differences in the surfaces of differently performing resonators.

Figure 4: Aging data for the three groups of studied resonators, frequency change vs time.

POST- AGING SURFACE ANALYSIS

After the resonators were aged a surface measurement was performed to determine if there were any significant differences between the surfaces of low to high aging resonators. The aging data shows that the groups of low, medium and high Cr layer thickness have relatively distinct performance differences and it was hoped that surface analysis might show a reason for these differences. To minimize the data set ten resonators were selected from each group and represented the best, middle and worst aging performances.

Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) was used to characterize the surface of each resonator after each device package was opened. A depth profile was performed by alternating analysis and sputtering to yield ToF-SIMS spectra as a function of depth. Data were acquired through the entire Au and underlying Cr adhesion layers. During acquisition, analysis was performed with a bunched 25kV Bi_1^+ primary ion beam while rastering over a $50 \times 50 \mu\text{m}^2$ area. The sputtering species during depth profile analysis was 2kV Cs^+ . Peak integrals corresponding to typical bulk and surface species were

plotted versus depth to create depth profiles for comparison. Additionally, surface spectra from the profile were used to determine relative surface composition.

Contaminates containing oxygen, carbon and chromium-dioxide CrO₂ were among the many elements and compounds measured on the surfaces of the aged resonator. Unfortunately no significant surface differences were found on resonators displaying significantly different aging rates. Figure 5 is an example of normalized CrO₂ thickness on the surface of resonators with aging rates shown on the X axis. One can see that this is essentially a scatter diagram in that the CrO₂ has no correlation to the resonator aging rate.

Figure 5: Surface measurement, normalized CrO₂ thickness vs. resonator aging rate.

CONCLUSIONS

The surface analysis was unable to find any significant differences in the surfaces of the aged resonators with relatively wide differing aging rates. Contaminates of carbon and CrO₂ were measured. The aging rates were grouped relatively tightly to the Cr thickness showing that the best performance was with middle thickness, 250Å. Since the aging of all groups over this 15 days was approximately 3.5ppm or less it is possible that the surface differences in these groups are too small to be measured with the technique chosen. It is likely that the differences between the three groups can simply be explained by the ability to control the construction process from group to group and that all these resonators were good performers and no large difference in the processes existed but since the resonator can “measure” extremely small mass changes over time the data is just showing the inability to make each group exactly the same.

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